



An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for *in situ* destruction of organic pollutants: Application to herbicide 2,4-D

M.A. OTURAN

Laboratoire d'Electrochimie Moléculaire, UMR-CNRS N° 7591, Université Paris 7 (Denis Diderot), 2 place Jussieu, 75251 Paris Cedex 05, France (e-mail: oturan@paris7.jussieu.fr; fax: +33 144 277625)

Received 17 February 1999; accepted in revised form 11 October 1999

Key words: 2,4-dichlorophenoxyacetic acid (2,4-D), Fenton's reagent, hydrogen peroxide, hydroxyl radical, total organic carbon (TOC), water treatment

Abstract

The electrochemical production of Fenton's reagent by simultaneous reduction of dioxygen and ferric ions on a carbon felt electrode, permits a controlled, *in situ* generation of hydroxyl (OH[•]) radicals. The possibility of using electrochemically produced OH[•] radicals for solving environmental problems is investigated. Continuous and controlled production of hydroxyl radicals was achieved by electrochemical reduction of O₂ in the presence of a catalytic amount of ferric or ferrous ion. These radicals are used for remediation of water containing toxic-persistent-bioaccumulative organic pollutants through their transformation into biodegradable compounds or through their mineralization into H₂O and CO₂. A widely used herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), was selected as a model for a toxic organic pollutant. High pressure liquid chromatography (HPLC) was used to quantify the distribution of the hydroxylated products obtained. Rate constants for the hydroxylation reactions of 2,4-D, 2,4-dichlorophenol (2,4-DCP), 2,4-dichlororesorcinol (2,4-DCR) and 4,6-dichlororesorcinol (4,6-DCR) were determined. The mineralization of 2,4-D and its derivatives was followed by total organic carbon (TOC) measurements. More than 95% of 2,4-D and the intermediates generated during the electrolysis can be mineralized.

1. Introduction

Removal of pollutants in drinking water may involve techniques such as flocculation, filtration and sterilisation procedures. One of the traditional purification methods involves activated carbon filtration. However, this technique only removes the pollutants; it does not destroy them. Biodegradation is an important water treatment method, but microorganisms leave intact many persistent organic contaminants. These physical or biological techniques may be coupled to chemical treatments which make use of a limited number of chemicals which are mostly precursors of highly reactive intermediates such as hydrogen peroxide, hydroxyl radical etc. which oxidize most of the organic species.

In the case of industrial or agricultural effluents and surface or ground water contamination by persistent (nonbiodegradable) organic pollutants, a chemical treatment is necessary in order to improve the quality of water resource which will be used for drinking. This treatment should eliminate toxic compounds before releasing the wastewater into natural cycles. Recent advances and technological improvements in this field have led to the development of oxidative degradation

procedures applying catalytic and photochemical methods known as advanced oxidation processes (AOPs) [1].

In recent years, interest in the use of electrochemical techniques for the destruction of nonbiodegradable organic toxics dissolved or dispersed in water has increased [2]. Direct electrochemical techniques for water purification involve the anodic [3–9] or cathodic [10–14] transformation of pollutants. Indirect electrochemical techniques involve electrogeneration of strong oxidants [15–17].

In this paper we describe an indirect electrochemical method for ecological treatment of water contaminated by organic pollutants. This method is based on an *in situ* and catalytic production of Fenton's reagent – a mixture of hydrogen peroxide H₂O₂ and ferrous iron Fe²⁺ – to produce hydroxyl radicals [18, 19] according to

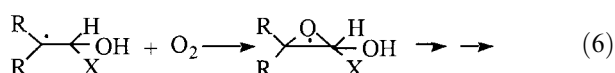
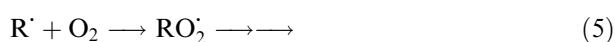


Many studies, including ours [20, 21] have shown that these radicals react very efficiently with organic compounds, finally leading to their destruction. Using these radicals in order to degrade industrial or agricultural toxic persistent organic pollutants therefore looks

very promising. In fact, hydroxyl radical is an extremely potent oxidising agent with a short life, which is able to oxidise organic compounds by hydrogen abstraction reaction (Equation 2), by redox reaction (Equation 3) or by electrophilic addition to π systems (Equation 4):



These reactions generate organic radicals, which by addition of molecular oxygen yield peroxy radicals, which in turn initiate chain reactions of oxidative degradation (Equations 5 and 6), leading finally to CO_2 and H_2O .



2,4-D is a widely used herbicide both in developed and developing countries (almost 100 millions kg per year in the United States, Europe and the Third World). Different methods have been used for the degradation of this herbicide: reductive electrochemical dechlorination [22, 23], chemical oxidation [24], photo-Fenton [25, 26], redox photodegradation [27, 28], electro-Fenton [29], photodecomposition [30, 31], and biodegradation [32–34]. All of these aim at the elimination of this pesticide under the best technical and economical conditions. With the same objective, we have studied hydroxyl radical production by electrochemical reduction of O_2 in aqueous solution containing 2,4-D. The mechanism and kinetics of the reaction between OH^\cdot radicals and 2,4-D have been examined. The hydroxylation of 2,4-D, the further evolution of hydroxylated derivatives and their transformation into water and carbon dioxide have been followed by high performance liquid chromatography (HPLC) and total organic carbon (TOC) measurements.

2. Experimental details

2.1. Chemicals

All the products were of commercial origin and were used without further purification. 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-dichlorophenol (2,4-DCP), 2,4-dichlororesorcinol (2,4-DCR), 4,6-dichlororesorcinol (4,6-DCR), 2-chloro 1,4-hydroquinone (2-CHQ), 2-chloro 1,4-benzoquinone (2-CBQ), 1,2,4-trihydroxybenzene (1,2,4-THB), salicylic acid (SA) and iron(III) chloride were purchased in the highest purity from Aldrich. Methanol (Chromanorm quality), sulphuric

acid (H_2SO_4) (Titrimorm grade) and other solvents were obtained from Prolabo. Carbon felt (working electrode material) was obtained from Carbone-Lorraine, molecular oxygen (O_2) from Carboxyque. Solutions were prepared with deionized water obtained from Millipore Milli-RO 6 system. The pH of initial solutions is set at 2 by addition of aqueous H_2SO_4 . The initial concentrations were: 0.5 to 2 mM for 2,4-D, 5 mM for 2,4-DCP, 2,4-DCR and 2,6-DCR. For kinetic studies all solutions were 1.0 mM.

2.2. Electrochemistry

Electrolyses were performed with an EG&G potentiostat/galvanostat (model 273A, Princeton Applied Research) and were carried out in a 150 mL three-electrode electrochemical cell. The working electrode was a 10 cm^2 piece of carbon-felt. A saturated calomel electrode (SCE, $E = 0.242$ V vs NHE) from Radiometer was used as reference electrode. The counter electrode was a 1 cm^2 platinum sheet (Radiometer). This electrode was placed in a cylindrical anodic compartment separated from the cathodic compartment by a glass frit of porosity 5.

The central anodic compartment contained only a 0.01 M H_2SO_4 solution. The volume of the aqueous 0.01 M H_2SO_4 solution containing the product to be oxidized was 125 mL. Prior to the electrolysis, dioxygen was bubbled for 5 min to saturate the aqueous solutions and then 12.6 mg of iron(III) chloride salt was introduced ($[\text{Fe}^{3+}] = 1$ mM), the solution was continuously agitated by a magnetic stirrer and dioxygen was bubbled through the solution during the electrolysis.

The controlled potential electrolysis were conducted at -0.50 V vs SCE, a potential which permits the simultaneous reduction of both dioxygen and Fe^{3+} (yielded by Fenton's reaction according to Equation 1) to superoxide ion ($\text{O}_2^{\cdot-}$) and ferrous ion (Fe^{2+}), respectively. Under these conditions the current remained constant (60 mA) and permitted a constant production of OH^\cdot radicals. The amount of charge passed through the solution is measured and displayed continuously by the EG&G galvanostat/potentiostat. The samples were withdrawn at regular charge intervals: 0, 50, 100, 200, etc. C for HPLC or TOC analysis.

2.3. HPLC

The decay of 2,4-D and change of the chemical composition of the solutions under study were followed by reverse-phase chromatography using a Gilson HPLC system, equipped with a u.v. detector (model 118) set at $\lambda = 280$ nm and fitted with a reverse phase Hypersil ODS 5 μm , 4.6 mm \times 25 cm column from Supelco Inc. This instrument was connected to a Macintosh LC 475 microcomputer which was controlled by a data acquisition and treatment software (Dynamax[®] from RAIN-IN Instrument Co. Inc.). A Rheodyne 7125 injector with

a 10 μL sample loop was used. Analyses were performed at room temperature and at isocratic mode where the mobile phase composition was: MeOH/H₂O/HAc: 58:40:2 v/v, with a flow rate = 0.5 mL min⁻¹.

Qualitative and quantitative analyses were performed by comparison with authentic samples. The calibration curves were established in a concentration range from 0.01 to 2.0 mM for 2,4-D and from 0.005 to 1.0 mM for 2,4-DCP, 2,4-DCR, 4,6-DCR, 2-CHQ and 2-CBQ. Product identification was conducted by retention time (t_R) comparison and internal standard addition methods under same conditions.

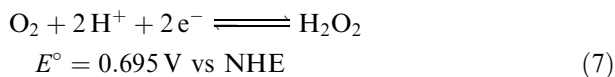
2.4. TOC analysis

Total organic carbon (TOC) measurements (thermal-catalytic oxidation principle) of initial and treated solutions were carried out by Analytik Jena GmbH using a IDC (Instrument Development Company) Micro N/C TOC analyser equipped with a ALS-C Autosampler. Samples were withdrawn from the electrolysis solution at different intervals. They were filtered and acidified by HCl and brought to pH 2 prior to analysis. The injection volumes were 100 μL . The temperature in the oven was 680 °C in combination with a Pt catalyst. Calibration of the analyser was achieved with potassium hydrogen phthalate standards (Merck).

3. Results and discussion

3.1. Electrochemically hydroxyl radicals production

Figure 1 shows schematically the principle of electrochemically production of OH[•] radicals. It is sufficient to apply a low cathodic potential (−0.5 V vs SCE, i.e. 0.255 V vs NHE) to the working carbon electrode to start the production of radicals. At this potential, dissolved dioxygen is reduced to superoxide ion ($\text{O}_2^{\cdot-}$) which reacts quickly with H⁺ in protic medium to produce peroxy radical HO_2^{\cdot} . This radical is unstable and leads through disproportionation to the formation of hydrogen peroxide:



At the applied potential which reduces O₂, a second cathodic reaction takes place simultaneously; the reduction of ferric ion to ferrous ion ($E^\circ = 0.77 \text{ V vs NHE}$):



The Fenton's reagent being thus electrochemically generated [21, 35–37], leads to the OH[•] radical production by the following homogeneous reaction in solution:

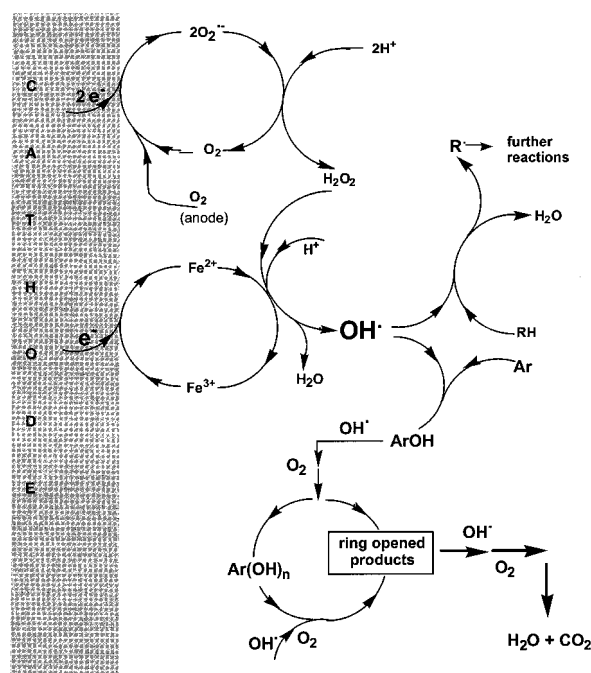
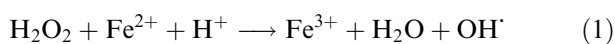
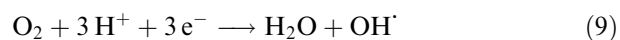
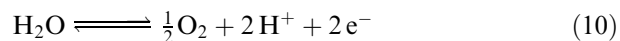


Fig. 1. Scheme of the electrocatalytic Fenton's reagent generation and homogenous OH[•] radical production in aqueous solution.

The sum of Reactions 7, 8 and 1 gives us the global reaction that takes place in the cathodic compartment:



In the anodic compartment, the reaction that takes place is simply the oxidation of water:



The evolution of oxygen on the surface of platinum electrode as well as the increasing of acidity in the anodic compartment can be observed during electrolysis.

Balanced overall reaction of electrochemical process taking place in the electrolysis cell and leading to the production of hydroxyl radicals is thus:



This overall reaction emphasises the catalytic character of this process: on one hand, the Fe²⁺ ion consumed by Reaction 1 is continuously regenerated on the cathode, on the other hand, 75% of the dioxygen required for the *in situ* formation of H₂O₂ is produced by oxidation of water at the anode (Figure 1). Thus the only reagents necessary for the production of two moles of OH[•] are half a mole of oxygen and energy (see the conclusion) from the electrical generator.

3.2. Degradation of 2,4-D and product analysis

The chromatographic survey by HPLC during the entire electrolysis permits to follow the chemical composition

of the solution as a function of the total charge consumed. Figure 2 shows the rapid decrease of 2,4-D (peak I) concentration in the aqueous solution as well as the very early appearing and rapidly increasing of a compound (peak II) with a retention time higher than 2,4-D (Table 1). This compound is the first hydroxylated derivative of 2,4-D, formed by attack of OH^\cdot radicals. At 50 C, new peaks appear which correspond to products III, IV, V and VI, and a group of peaks, with a retention time (t_R) of 5–8 min.

Products II–V are identified (Table 1) by comparison of their HPLC retention times with those of authentic samples. During the course of the electrolysis, the concentration of products II–VI increase, reach a maximal value and then decrease. This indicates that these products are in turn attacked by hydroxyl radicals and their maximum corresponds to a stationary state where the rate of reaction with hydroxyl radicals equals their rate of formation from 2,4-D. This behaviour is exemplified on Figure 3 in the case of the three hydroxylated derivatives of 2,4-D: 2,4-DCP, 2,4-DCR and 4,6-DCR.

Table 1. Hydroxylation products of 2,4-D identified by HPLC analysis (see experimental section for analysis conditions)

Peak n°	t_R (min)	Identification	Chemical formula
I	22.15	2,4-D	
II	25.17	2,4-DCP	
III	17.83	2,4-DCR	
IV	12.67	4,6-DCR	
V	10.92	2-CHQ	
VI	10.23	2-CBQ	
VII	6.34	1,2,4-THB	

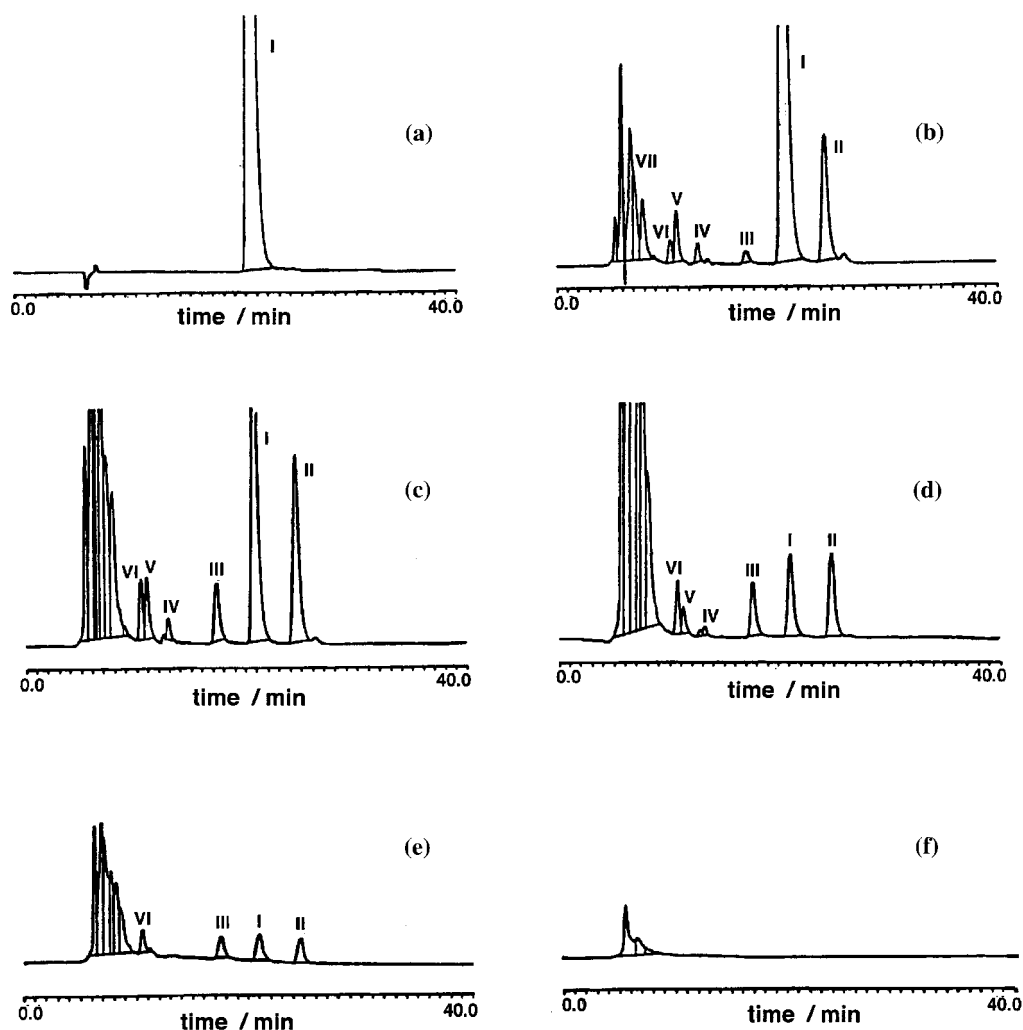


Fig. 2. Reverse-phase HPLC chromatograms (detection at 280 nm) of a 125 mL aqueous solution containing initially 2.0 mM of 2,4-D. Evolution of product distribution with total charge consumed during degradation of 2,4-D by electrochemically generated OH^\cdot radicals. (a) 0 C, (b) 50 C, (c) 150 C, (d) 300 C, (e) 500 C, (f) 700 C. For compound numbers see Table 1.

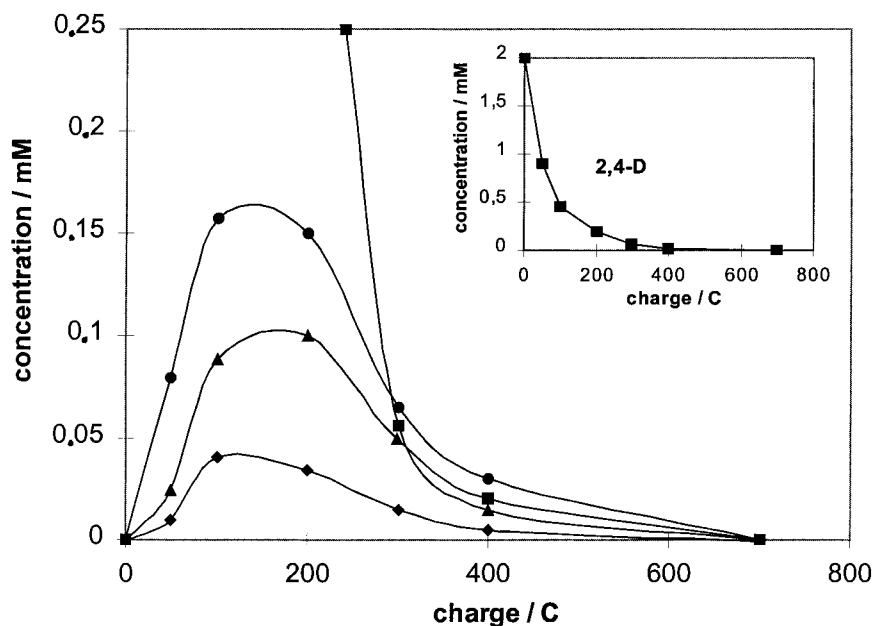
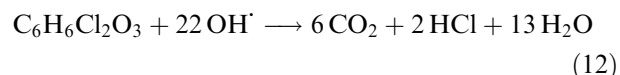


Fig. 3. Hydroxylation of 2,4-D and variation of the concentration of some of its derivatives during electrolysis as function of electric charge passed. Key: (■) 2,4-D, (●) 2,4-DCP, (▲) 2,4-DCR, (◆) 4,6-DCR. Initial concentration of 2,4-D was 2.0 mM and the volume of solution was 125 mL.

At 500 C there are no aromatic compounds left in the solution and at 700 C, the chromatogram is almost reduced to a straight base line (Figure 2), indicating that the possible (unsaturated) aliphatic compounds (with retention time between 5 and 8 min) are also degraded.

3.3. TOC removal

Electrolysis of solutions (125 mL) initially containing 1 mM (220 ppm) of 2,4-D leads to a gradual decrease in TOC with electrolysis time. Figure 4 shows the TOC decay during the controlled potential electrolysis under conditions described in the experimental section and with a current $I = 60$ mA. The percentage of TOC removal was 33, 52, 65 and 76 for 60, 120, 180 and 240 min, respectively. At 2000 C the quantity of organic matter which is present in the solution is less a 7% of the initial quantity of 2,4-D. Moreover, as indicated by the chromatographic analysis, this organic matter is composed of aliphatic compounds. Thus the toxicity of the initial molecule has been eliminated by the ring opening reactions of the aromatic hydroxylated intermediates. This TOC decay is related to the mineralization (transformation into $\text{H}_2\text{O} + \text{CO}_2$) of the herbicide 2,4-D in the presence of electrochemically generated OH^\cdot radicals. The rate of mineralization is high at the beginning of the electrolysis; it diminishes towards the end. Casado et al. [12] have observed a similar behaviour during the photoelectro-Fenton process in the case of 4-chlorophenol. These results indicate that 2,4-D is mineralized by electrochemically produced OH^\cdot radicals yielding CO_2 , H_2O and HCl . The mineralization reaction can be written as follows:



The apparent current efficiency (ACE) at a given time is obtained from the following equation:

$$\text{ACE} = \frac{\Delta(\text{TOC})_{\text{exp}}}{\Delta(\text{TOC})_{\text{theo}}} \times 100 \quad (13)$$

where $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay ($[\text{TOC}]_0 - [\text{TOC}]_t$) and $\Delta(\text{TOC})_{\text{theo}}$ is the theoretically calculated TOC decay assuming that the applied electrical charge is completely used for Reaction 12. Figure 4 permits to determine the apparent current efficiency. It was 44% at 150 C (40 min). A progressive decrease was observed throughout the process: 37% at 500 C (140 min) and 27% 1000 C (280 min) under experimental conditions.

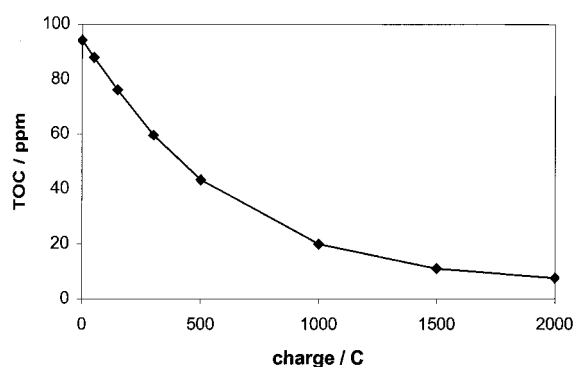


Fig. 4. TOC decay with total charge passed during the mineralization of a 125 mL aqueous solution containing 220 ppm (1 mM) of 2,4-D.

3.4. Determination of the initial rate constants

Under our experimental conditions (saturated aqueous solution $[O_2] = 1.3 \text{ mM}$, $I = 60 \text{ mA}$) the rate of production of OH^\bullet is electrochemically controlled and constant. As it is a species with a very short life, the quasi-stationary state can be applied to hydroxyl radical concentration and consequently the hydroxylation reactions are pseudo first order reactions in terms of substrate.

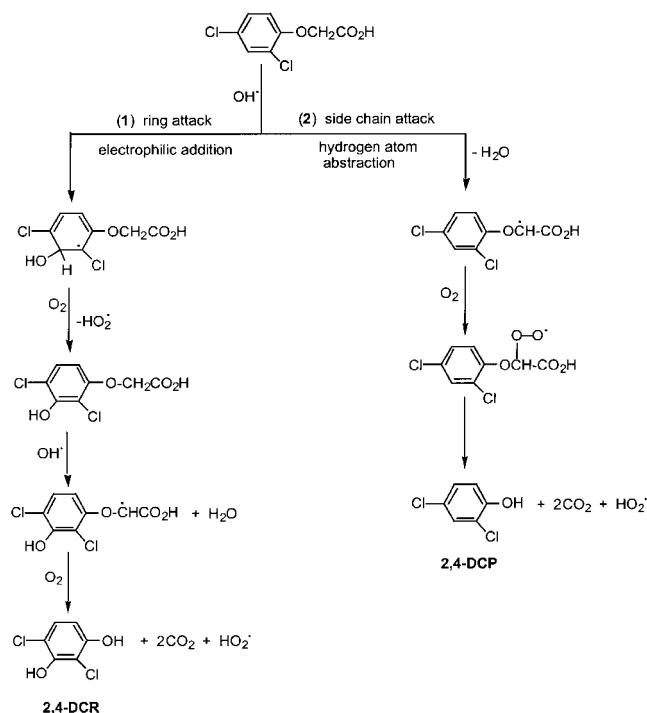
The relative rate constants for hydroxylation reaction of 2,4-D, 2,4-DCP, 2,4-DCR and 4,6-DCR were determined by reference to salicylic acid ($k = 2.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) [38] which is a well known trap for OH^\bullet radicals. A mixture of salicylic acid ($C_0 = 1 \text{ mM}$, $V = 125 \text{ mL}$) and the substrate under examination ($C_0 = 1 \text{ mM}$, $V = 125 \text{ mL}$) was electrolysed and their relative concentrations were measured by HPLC at the beginning of the electrolysis at 5 C. The relative rate constants found were 1.57, 1.52, 1.45 and 1.76 for 2,4-D, 2,4-DCP, 2,4-DCR and 4,6-DCR respectively, close to the diffusion limited rate constants. These relative rate constants confirm the product distribution during electrolysis (cf. Figure 2) and indicate that not only 2,4-D but all of the intermediates formed during its degradation are transformed to CO_2 and H_2O with high initial rate constants through hydroxylation and ring opening reactions. This is obviously one of the interesting results of this procedure.

3.5. Mechanistic considerations

The reaction mechanism of OH^\bullet radicals with aromatic compounds has been previously investigated [21, 39–44]. The first step is the fast electrophilic addition ($k \approx 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) of hydroxyl radical on to the aromatic ring, leading to the formation of a cyclohexadienyl radical. This radical can undergo different types of reactions as dimerisation, disproportionation, oxidation, etc. according to the characteristics of the reaction medium. Under our conditions, in the presence of dioxygen, the reaction medium is oxidising; therefore the oxidation reaction leading to the formation of hydroxylated compounds should dominate. However the product analysis of the reaction mixture with respect to 2,4-D, shows that this reaction is simultaneously accompanied by the cleavage of the side chain. Two reaction pathways take place simultaneously and lead to the formation of the dichlorophenols (Scheme 1).

The kinetic data (cf. Section 3.4) indicate that the dichlorophenols 2,4-DCP and 2,4-DCR are also as reactive towards the OH^\bullet radicals as the 2,4-D. A second electrophilic attack of the OH^\bullet radical leads to the formation of the dihydroxylated derivatives [21], among which the 4,6-DCR (Scheme 2).

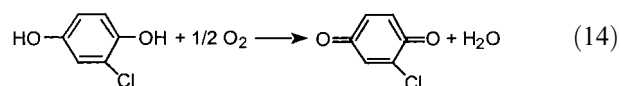
The formation of the 2-CHQ and 2-CBQ suggests the existence of a dechlorination process. An ipso attack of the OH^\bullet radical on the chlorine position leading to



Scheme 1. Proposed reaction pathways for the formation of 2,4-DCP and 2,4-DCR by the hydroxylation of 2,4-D.

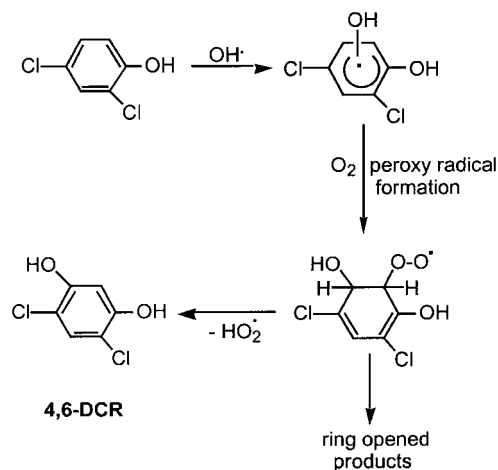
cyclohexadienyl radical may provoke departure of chlorine (Scheme 3).

Formation of quinones is a common observation of the hydroxylation processes in oxidising media. The 2-CBQ is formed by the oxidation of the 2-CHQ:

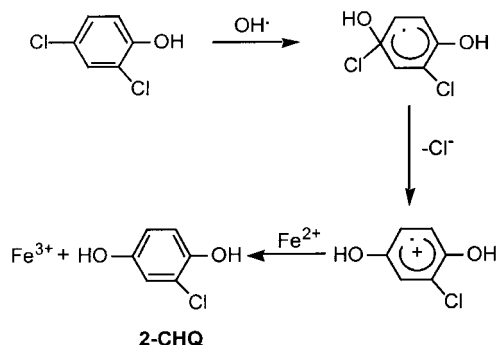


The dechlorination of 2-CHQ leads to formation of 1,2,4-THB by a similar process shown by Scheme 3.

Many recent studies [12, 26, 44–46] dealing with the reaction of hydroxyl radicals produced by pulse



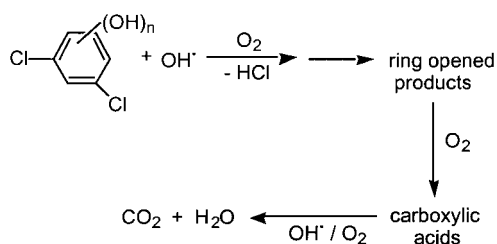
Scheme 2. Proposed reaction pathway for the formation of 4,6-DCR from 2,4-DCP.



Scheme 3. Proposed reaction pathway for the formation of 2-CHQ from 2,4-DCP.

radiolysis, photochemistry or by Fenton reaction have shown the instability of the hydroxylated aromatic compounds in presence of these radicals. Sun and Pignatello [26] have reported the mineralization of 2,4-D by photochemically produced OH^\cdot radicals. von Sonntag et al. [45] and Casado et al. [12] have recently studied the degradation of 4-chlorophenol by OH^\cdot radicals leading to the cleavage of the aromatic ring, accompanied by the leaving of chlorine atom. The mineralization mechanism which can be summarized by Scheme 4 is indeed very complex. It consists of a chain reaction involving different reactive oxygen species.

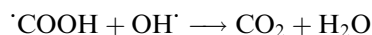
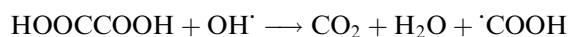
The group of peaks observed at the beginning of the HPLC chromatograms is due to the presence of the polar compounds in the solution. These compounds which are formed by ring opening reaction of hydroxylated derivatives have been previously identified as carboxylic acids, aliphatic alcohols, aldehydes or esters. Maleic and fumaric acids have been identified in the case of the 4-chlorophenol [12] and in the case of the 2,4-D, oxalic acid was observed [26]. Mineralization reaction pathways by OH^\cdot attacks of some carboxylic acids such as formic, acetic, glycolic, oxalic etc. and of 1,2-ethanediol monoformate ($\text{O}=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$) and 1,2-ethanediol diformate ($\text{O}=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}=\text{O}$) were also reported [47]. The TOC (Figure 4) and chromatographic (Figure 2) analysis results show that mineralization of aliphatic compounds by OH^\cdot radicals is slower than that the hydroxylation of aromatics.



Scheme 4. Mineralization pathway for hydroxylated derivatives of 2,4-D.

4. Conclusion

We have demonstrated that the first stable products formed by the reaction of OH^\cdot radicals with 2,4-D are dichlorophenols. The hydroxylation reaction is accompanied by the cleavage of the C—O bond of the phenoxy group. Further reaction of these products with loss of chloride ions form carboxylic acids which oxidize to oxalic acid before undergoing a rapid mineralization:



This particular example of 2,4-D shows that destruction of organic contaminants by electrochemically generated OH^\cdot radicals is a very clean procedure, well suited to the treatment of water contaminated by toxic-persistent-bioaccumulative organic pollutants. The method is an efficient and ecologically friendly and uses a clean energy source (electricity). Catalytic quantity of a soluble salt of iron(II) or iron(III) is the only chemical reagent added to the medium. No chemicals are produced to be extracted after the treatment. The process needs only a simple direct current generator instead of costly chemicals, resulting a low cost and non-polluting method for *in situ* destruction of toxic persistent organic pollutants. For example, complete mineralization (cf. TOC results and Figure 2) of 125 mL solution of 2,4-D (2 mg L^{-1}) needs 1000 C. In terms of electrical energy, this quantity corresponds to $5.5 \times 10^{-4} \text{ kW h}$. Given the price of electrical energy (0.08 \$ per kW h), the cost of treatment remains very low even if large volumes are processed. However the current density of superoxide ion and related H_2O_2 production is limited by the solubility of oxygen in aqueous solution. In order to increase the efficiency of the method, use of a gas diffusion electrode [48] seems a suitable procedure.

Combining this process with biological treatments, one can even further reduce the cost. One can stop the electrolysis when no aromatic products remain in the solution. The resulting ring opening compounds being biodegradable, a biological process can thus complete mineralization.

Use of electrochemically generated OH^\cdot radicals to destroy organic pollutants provides an ecologically friendly water treatment technique which can therefore be considered as a serious alternative method for wastewater treatment and as such can compete other methods such as photochemical, radiolysis, Fenton's reagent.

Acknowledgement

The author gratefully acknowledges helpful discussions with Professor J. Pinson, Dr P. Boule, Professor T. Ozgen and technical assistance from Dr N. Oturan. He is grateful to Dr O. Kampe (Analytik Jena GmbH), B. Yurdakul and L. Joubert (Perichrom sarl) for performing the TOC analysis.

References

1. O. Legrini, E. Oliveros and A.M. Braun, *Chem. Rev.* **93** (1996) 671.
2. P.M. Bersier, L. Carlsson and J. Bersier, *Electrochemistry for a better environment*, in 'Topics in Current Chemistry, Electrochemistry, V' (Springer Verlag, 1994).
3. J. Gassmann, J. Voss and G. Adiwidjaja, *Z. Naturforsch.* **50b** (1995) 953.
4. P.L. Cabot, M. Centelles, L. Segarra and J. Casado, *J. Electrochem. Soc.* **144** (1997) 3749.
5. S. Stucki, R. Kötzt, B. Carcer and W. Suter, *J. Appl. Electrochem.* **21** (1991) 99.
6. C. Pulgarin, N. Adler, P. Peringer and Ch. Comninellis, *Wat. Res.* **28** (1994) 887.
7. Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **21** (1991) 703.
8. Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **23** (1993) 108.
9. N.B. Tahar and A. Savall, *J. Electrochem. Soc.* **145** (1998) 3427.
10. O. Kargina, B. MacDougall, Y.M. Kargin and L. Wang, *J. Electrochem. Soc.* **144** (1997) 3715.
11. P. Ribordy, C. Pulgarin, J. Kiwi and P. Péringer, *Water Sci. Tech.* **35** (1997) 293.
12. E. Brillas, R. Saulea and J. Casado, *J. Electrochem. Soc.* **145** (1998) 759.
13. I.F. Cheng, Q. Fernando and N. Korte, *Environ. Sci. Technol.* **31** (1998) 1074.
14. A.I. Tsyganok, I. Yamanaka and K. Otsuka, *Chem. Lett.* (1988) 303.
15. Ch. Comninellis and A. Nerini, *J. Appl. Electrochem.* **25** (1995) 23.
16. Y.L. Hsiao and K. Nobe, *J. Appl. Electrochem.* **23** (1993) 943.
17. O. Koyama, Y. Kamagata and K. Nakamura, *Water Res.* **28** (1994) 895.
18. H.J.F. Fenton, *J. Chem. Soc.* **65** (1894) 8234.
19. C. Walling, *Acc. Chem. Res.* **8** (1975) 125.
20. M.A. Oturan, J. Pinson, D. Deprez and B. Terlain, *New J. Chem.* **16** (1992) 705.
21. M.A. Oturan and J. Pinson, *J. Phys. Chem.* **99** (1995) 13948 and references cited therein.
22. A. Tsyganok, K. Otsuka, I. Yamanaka, V. Plekhanov and S. Kulikov, *Chem. Lett.* **4** (1996) 261.
23. D.C. Coomber, D.J. Tucker and A.M. Bond, *J. Electroanal. Chem.* **426** (1997) 63.
24. Y. Sun and J.J. Pignatello, *J. Agric. Food Chem.* **40** (1992) 322.
25. R. Bauer and H. Fallmann, *Res. Chem. Intermed.* **23** (1997) 341.
26. Y. Sun and J.J. Pignatello, *Environ. Sci. Technol.* **27** (1993) 304.
27. L. Sanchez, J. Peral and X. Domenech, *Electrochim. Acta* **41** (1996) 1981.
28. M. Trillas, J. Peral and X. Domenech, *Appl. Catal. B* **5** (1995) 377.
29. M.A. Oturan, J.J. Aaron, N. Oturan and J. Pinson, *Pestic. Sci.* **55** (1999) 558.
30. P. Pichat, J.C. D'Oliveira, J.F. Maffreand and D. Mas, *Trace Met. Environ.* **3** (1993) 683.
31. M. Trillas, L. Sanchez, J. Peral and X. Domenech, *Proc. Electrochem. Soc.* (1994) 290.
32. E. Camarro and S. Esplugas, *J. Chem. Technol. Biotechnol.* **57** (1993) 273.
33. G.S. Kochar and R.S. Kahlon, *J. Gen. Appl. Microbiol.* **41** (1995) 367.
34. B. Kuhlmann and B. Kaczmarczyk, *Environ. Toxicol. Water Qual.* **10** (1995) 119.
35. R. Tomat and A. Rigo, *J. Appl. Electrochem.* **9** (1979) 301.
36. R. Tomat and A. Rigo, *J. Appl. Electrochem.* **14** (1984) 1.
37. T. Tzedakis, A. Savall and M.J. Clifton, *J. Appl. Electrochem.* **19** (1989) 911 and references cited therein.
38. G.V. Buxton, C.L. Greenstock, W.P. Helman and A.B. Ross, *J. Phys. Chem. Ref. Data* **17** (1988) 513.
39. M.A. Oturan, J. Pinson, J. Bizot, D. Deprez and B. Terlain, *J. Electroanal. Chem.* **334** (1992) 103.
40. M.K. Eberhardt and M.L. Martinez, *J. Phys. Chem.* **79** (1975) 1917.
41. M.K. Eberhardt, *J. Phys. Chem.* **81** (1975) 1051.
42. J.R. Lindsay Smith and R.O.C. Norman, *J. Chem. Soc.* (1963) 2897.
43. N.V. Raghavan and S. Steenken, *J. Am. Chem. Soc.* **102** (1980) 3495.
44. X-M. Pan, M.N. Schuchmann and C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* (1993) 289.
45. G. Merga, H-P. Schuchmann, B.S. Madhava Rao and C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* (1996) 1097.
46. A.B. Thomsen, *Water Res.* **32** (1998) 136.
47. M.I. Stephan and J.R. Bolton, *Environ. Sci. Technol.* **32** (1998) 1588.
48. E. Brillas, R.M. Bastida, E. Llosa and J. Casado, *J. Electrochem. Soc.* **142** (1995) 1733.